Photocatalytic Reduction of CO_2 with H_2O on Titanium Oxides Prepared within the FSM-16 Mesoporous Zeolite

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Highly dispersed titanium oxide catalysts have been prepared within the mesoporous cavities of the FSM-16 zeolite (Ti-oxide/FSM-16 catalyst) by a CVD method and utilized for the photocatalytic reduction of CO_2 with H_2O to produce CH_4 and CH_3OH at 328 K. These Ti-oxide/FSM-16 photocatalysts exhibited high reactivity and selectivity for the formation of CH_3OH, its reactivity and selectivity showing a good relationship with the photoluminescence yield of the catalyst which can be attributed to the radiative decay from the charge transfer excited state of the tetrahedral coordinated titanium oxides.

In recent years, the development and application of titanium oxide-based photocatalysts to deal with environmental pollution have been one of the most active areas of research in heterogeneous photocatalysis.[1] The fixation of CO_2 with H_2O using a highly reactive photocatalyst is of special interest not only for the transformation and storage of unlimited solar energy into useful chemical energy but also in developing ways to recycle the earth's limited carbon resources. In order to achieve these specific objectives, titanium oxides have been widely and successfully used.[2-5]

Various fundamental studies in the photocatalytic reduction of CO_2 with H_2O on highly active titanium oxides have been carried out and we have reported on the UV-irradiation of Ti-MCM-41 and Ti-MCM-48 zeolites as well as titanium oxide photocatalysts prepared within Y-zeolite cavities by an ion-exchange method in the presence of CO_2 and H_2O at room temperature. This led to the highly selective formation of CH_3OH, its selectivity greatly depending on the dispersion state and local structure of the titanium oxide species.[6-11] In the present study, highly dispersed titanium oxide species have been prepared within the mesoporous cavities of the FSM-16 zeolite by the CVD method and has been applied as a photocatalyst for the reduction of CO_2 with H_2O.

The FSM-16 zeolite was synthesized according to procedures reported in previous literature.[12] Anchoring of the Ti ions onto the zeolite was performed through a facile reaction of $TiCl_4$ with the surface hydroxyl groups of FSM-16 in the gas phase at 453-473 K, followed by treatment with water vapor to replace the chlorine atoms with the OH groups.[13,14] After these treatments, the samples were evacuated and then calcined in oxygen at 753 K for 5 h. The number of surface OH groups on the FSM-16 zeolite was controlled by varying the degassing temperature within a range from 573 K to 873 K, since the correlation between the number of remaining surface OH groups and the degassing temperature is well established.[15]

Prior to photoreactions and spectroscopic measurements, the catalysts (50 mg) were heated in O_2 at 723 K for 2 h and then evacuated at 475 K for 1 h. UV irradiation of the catalysts in the presence of CO_2 (24 μmol) and gaseous H_2O (120 μmol) was carried out using a high-pressure Hg lamp (Toshiba SHL 100 W, $\lambda > 280$ nm) for 6 h at 323 K. The reaction products collected in the gas phase were analyzed by gaschromatography.

The absorption spectra of the Ti-oxide/FSM-16 photocatalysts and a bulk TiO_2 reference catalyst were measured by the UV diffuse reflectance method. Figure 1 shows the UV-vis spectra of the Ti-oxide/FSM-16 catalysts. The absorption spectra of the catalysts are observed at shorter wavelength regions as compared to that of the bulk TiO_2 catalyst. Moreover, when the Ti-oxide catalysts were prepared on FSM-16 degassed at a higher temperature, the absorption edge of the catalysts can be observed to shift to shorter wavelength regions with the increase in the degassing temperature (Figure.1. a → d). These results clearly suggest that the dispersion state of the Ti-oxide species on the catalyst become higher with the rise of the pretreatment temperature of the FSM-16 zeolite before the CVD reaction, i. e., with the decrease in the number of surface OH groups on FSM-16.

UV irradiation of the Ti-oxide/FSM-16 catalysts in the presence of a mixture of CO_2 and H_2O led to the evolution of CH_4 and CH_3OH in the gas phase at 323 K, as well as to the formation of trace amounts of CO, C_2H_4, and C_2H_6. The evolution of small amounts of O_2 could also be observed. The

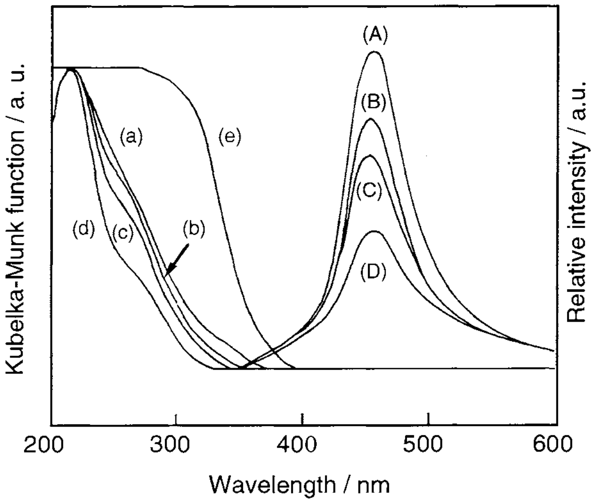

Figure 1. The diffuse reflectance spectra of Ti-oxide/FSM-16<573> (a),Ti-oxide/FSM-16<673> (b), Ti-oxide/FSM-16<773> (c), Ti-oxide/FSM-16<873> (d) and anatase TiO_2 powder as a reference (e) as well as the Photoluminescence spectrum of the Ti-oxide/FSM-16(873) and the effect of the addition of CO_2 or H_2O on the spectrum. (A) 0, (B) CO_2; 1.0 Torr, (C) H_2O; 1.0 Torr, (D) H_2O 5.0 Torr. (UV diffuse reflectance spectra were measured at 295 K. Photoluminescence spectra were measured at 77 K. Excitation wavelength was 280 nm ±5 nm.)

yields of these photoformed products increased in parallel with the irradiation time (~60 h). Without the catalyst or under dark conditions, no products could be detected. Investigations of the effects of the pretreatment temperature of FSM-16 on the yields of the formation of CH_4 and CH_3OH on Ti-oxide/FSM-16 clearly showed that the formation of CH_3OH is remarkably enhanced when the degassing temperature is increased while the yield of CH_4 decreases slightly. Furthermore, the selectivity of CH_3OH formation was found to become higher when the degassing temperature of FSM-16 is increased. Thus, these results clearly suggest that a high photocatalytic efficiency and selectivity for the formation of CH_3OH in the photocatalytic reduction of CO_2 with H_2O could be achieved by the design of catalysts having highly dispersed Ti-oxide species within the mesoporos cavities of the FSM-16 zeolite. Such reactivity and selectivity for the formation of CH_3OH was found to be much higher than with Ti-MCM-41 and Ti-MCM-48.[8]

As can also be seen in Figure.1, the Ti-oxide/FSM-16 catalyst exhibited a photoluminescence spectrum at around 450-600 nm by excitation at around 260-290 nm at 77 K. These observed absorption and photoluminescence spectra are attributed to the charge transfer absorption process on the tetrahedrally coordinated titanium oxides and the reverse radiative decay process from the charge transfer excited state (Ti^{3+} - O^-)* to the ground state (Ti^{4+} - O^{2-}) of the highly dispersed titanium oxide species having a tetrahedral coordination, respectively.[7-10]

As shown in Figure. 1, the addition of H_2O or CO_2 molecules onto the Ti-oxide/FSM-16 catalysts leads to the quenching of the photoluminescence with different efficiencies. The lifetime of the charge transfer excited state of the Ti-oxides was found to be shortened from 0.53 ms to 0.36 ms by the addition of CO_2 at 1.0 Torr and to 0.28 ms by the addition of H_2O at 1.0 Torr, the extent depending on the amount of added molecules. Such an efficient quenching of the photoluminescence with the added CO_2 or H_2O clearly suggests that these molecules interact with the charge transfer excited state of the tetrahedrally coordinated titanium oxide species.

The relationship between the yields of the photoluminescence spectrum which can be attributed to the charge transfer excited state of the tetrahedrally coordinated titanium oxides and the yield of the formation of CH_3OH in the photocatalytic reduction of CO_2 with H_2O is shown in Figure. 2. The yields of CH_3OH formation increase when the yields of the photoluminescence of the catalysts increase. These results clearly suggest that the charge transfer excited complexes of the tetrahedrally coordinated titanium oxide species formed under UV irradiation of the catalysts play a significant role in the formation of CH_3OH. This novel approach clearly shows the relationship between the yield of the charge transfer excited triplet state of the tetrahedral coordinated titanium oxides and the yield of CH_3OH from CO_2 and H_2O. Taking into consideration the presence of optimum conditions in the ratios of CO_2/H_2O for the highest yield and selectivity in the formation of CH_3OH, it seems the competitive co-adsorption of H_2O and CO_2 on the tetrahedrally coordinated titanium oxides is crucial for the reaction.

In summary, we were able to prepare Ti-oxide/FSM-16 zeolite catalysts by applying the CVD method to dehydrated FSM-16 systems. The dispersion level of the titanium oxides was controlled by varying the degassing temperature of FSM-16 before applying the CVD reaction. The photocatalytic reduction of CO_2 with H_2O on the Ti-oxide/FSM-16 catalysts led to a high selectivity for the formation of methanol while its selectivity was closely related to the dispersion level and the yields of the photoluminescence due to the presence of highly dispersed titanium oxides having a tetrahedral coordination.

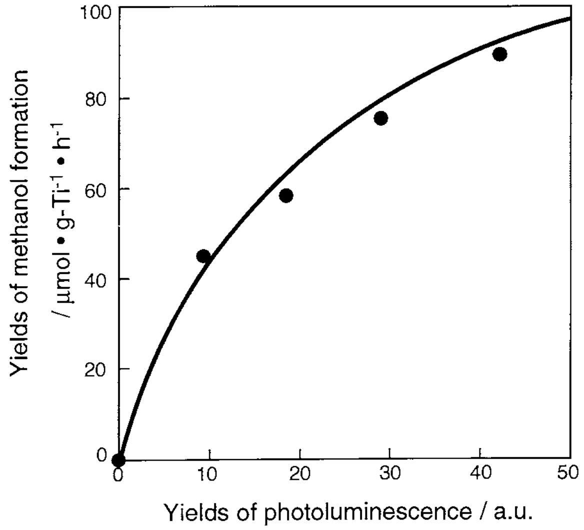

Figure 2. The relationship between the yields of the photoluminescence due to the tetrahedrally coordinated titanium oxides and the yields of the CH_3OH formation in the photocatalytic reduction of CO_2 with H_2O on the Ti-oxide/FSM-16 catalysts.(Ti contents; 0.019~0.025 wt%, the volume of the reactor; 85 cm^3, BET surface area; 650~750 m^2/g)

References

1 M. Anpo, in "Protecting the Environment," BHR Group, London (1998), pp. 75-88, and references therein.
2 T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature*, **277**, 637 (1979).
3 O. Ishitani, C. Inoue, Y. Suzuki, and T. Ibusuki, *J. Photochem. Photobiol. A: Chem.*, **72**, 269 (1993).
4 F. Saladin, L. Forss, and I. Kamber, *J. Chem. Soc., Chem. Commun.*, **1995**, 533.
5 F. Saladin and I. Alxneit, *J. Chem. Soc., Faraday Trans.*, **93**, 4159 (1997).
6 M. Anpo and K. Chiba, *J. Mol. Catal.*, **74**, 207 (1992).
7 M. Anpo, H. Yamashita, Y. Ichihashi, Y. Fujii, and M. Honda, *J. Phys. Chem. B*, **101**, 2632 (1997).
8 S. G. Zhang, Y. Fujii, H. Yamashita, K. Koyano, T. Tatsumi, and M. Anpo, *Chem. Lett.*, **1997**, 659.
9 M. Anpo, H. Yamashita, K. Ikeue, Y. Fujii, Y. Ichihashi, S. G. Zhang, D. R. Park, S. Ehara, S. E. Park, J. S. Chang, and J. W. Yoo, *Stud. Surf. Sci. Catal.*, **114**, 177 (1998).
10 M. Anpo, H. Yamashita, K. Ikeue, Y. Fujii, S. G. Zhang, Y. Ichihashi, D. R. Park, Y. Suzuki, K. Koyano, and T. Tatsumi, *Catal. Today*, **44**, 327 (1998).
11 H. Yamashita, Y. Fujii, Y. Ichihashi, S. G. Zhang, K. Ikeue, D. R. Park, K. Koyano, T. Tatsumi, and M. Anpo, *Catal. Today*, **45**, 221 (1998).
12 S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima, and K. Kuroda, *Bull. Chem. Soc. Jpn.*, **69**, 1449 (1996).
13 M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, and E. Giamello, *J. Phys. Chem.*, **89**, 5017 (1985).
14 M. Anpo, *Catal. Surv. Jpn.*, **1**, 169 (1997).
15 M. J. D. Low and N. Ramasubramanian, *J. Phys. Chem.*, **71**, 730 (1967).